ARS-33-135
March 1970

ALDICARB RESIDUES IN APPLES, PEARS, SUGARBEETS, AND COTTONSEED; PERFORMANCE IN APPLES AND PEARS

Agricultural Research Service

UNITED STATES DEPARTMENT OF AGRICULTURE

This publication reports research involving pesticides. It does not contain recommendations for their use, nor does it imply that the uses discussed here have been registered. All uses of pesticides must be registered by appropriate State and/or Federal agencies before they can be recommended.

CAUTION: Pesticides can be injurious to humans, domestic animals, desirable plants, and fish or other wildlife -- if they are not handled or applied properly. Use all pesticides selectively and carefully. Follow recommended practices for the disposal of surplus pesticides and pesticide containers.

Trade names are used in this publication solely for the purpose of providing specific information. Mention of a trade name does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture or an endorsement by the Department over other products not mentioned.

ALDICARB RESIDUES IN APPLES, PEARS, SUGARBEETS, AND COTTONSEED; PERFORMANCE IN APPLES AND PEARS

By J. C. Maitlen, L. M. McDonough, F. Dean,
B. A. Butt, and B. J. Landis
Entomology Research Division

Aldicarb, 2-methyl-2-(methylthio)propionaldehyde O-(methylcarbamoyl) oxime, has shown promise of controlling a variety of insects including species in the orders Thysanoptera, Homoptera, Coleoptera, Diptera, and Hemiptera. It has also been used successfully against mites and nematodes but is not effective against lepidopterous insects (1).[1/]

The LD_{50} (lethal dose to 50 percent of test species) of aldicarb to rats is 0.93 milligram per kilogram of body weight when it is given orally (10). In comparison, the LD_{50} of parathion is 5 mg. per kg. (4). Because of its high mammalian toxicity, aldicarb is applied only as a 10 percent granular formulation (Temik)[2/] produced by impregnating the granules with a mixture of an organic carrier, aldicarb, and a water-soluble sticking agent to minimize "dusting."

Chemically, aldicarb is a carbamoyloxime containing a sulfide linkage. Metcalf and others (7) determined that the metabolites of aldicarb in cotton and in houseflies, Musca domestica L., were the same. Two principal reactions account for the five metabolites: oxidation of the sulfide to give aldicarb sulfoxide and aldicarb sulfone and hydrolysis of the carbamoyloximes to give aldicarb oxime, aldicarb sulfoxide oxime, and aldicarb sulfone oximes. The last three metabolites have no significant toxicity to either mammals or insects, but in houseflies, aldicarb sulfoxide is 76 and aldicarb sulfone is 17 times more potent as cholinesterase inhibitors than aldicarb. Obviously, an analytical method that measures all the toxic residues without interference from the nontoxic residues was needed. The method of Maitlen and others (6) satisfied these conditions and was used.

The data in this report were obtained from studies that had the dual purpose of evaluating the efficacy of aldicarb against various pests and of determining the kind and amount of toxic residues resulting when various amounts of aldicarb are applied. The evaluation of the efficacy of aldicarb in sugarbeets and cotton will be published elsewhere. Residues and performance of aldicarb in oranges (9) and in alfalfa (8) have been reported.

1/ Underscored numbers in parentheses refer to Literature Cited at the end of this report.

2/ Manufactured by the Union Carbide Corp. as UC-21149.

INSECTICIDE TREATMENT, GROWING, SAMPLING, AND SAMPLE PREPARATION

Apples

On May 9, 1966, aldicarb was applied to the soil around three plots of apple trees in Yakima, Wash., at the rate of 0.1, 0.2, and 0.4 pounds of active ingredient per tree, which was immediately washed into the soil by sprinkler irrigation. The control plot and the three treated plots consisted of two trees each.

At harvesttime, September 29, 143 days after treatment, samples of apples were taken at random from the two trees in each plot and composited into one sample (about 8 pounds). At the laboratory, one-quarter of each of 20 apples from the four plots were finely diced and frozen immediately.

Three subsamples of 150 grams were taken from each of the diced composite samples, and blended for 4 minutes with 4 g. of an adsorbent mixture, 60 to 70 g. of anhydrous sodium sulfate, and 450 milliliters of distilled chloroform. The adsorbent mixture consisted of equal parts of Nuchar-C-190-N, aluminum oxide, Florisil, and 1:1 magnesium oxide-Hyflo Super Cel. The blended mixture was filtered through a glass wool plug into a flask containing 60 to 70 g. of sodium sulfate, shaken, and then filtered through a funnel containing a cotton plug overlaid with sodium sulfate. The solution (300 ml.), which was equivalent to 100 g. of sample, was evaporated to dryness in a water bath (40° C.) with the aid of a gentle stream of air, and the residue was dissolved in 15 ml. of acetonitrile.

Pears

On May 6, 1966, aldicarb was applied to the soil around three plots of pear trees in Yakima, Wash., at the rates of 1, 2, and 4 ounces of active ingredient per tree. The subsequent procedure was identical to that used with apples, except that samples were taken from each of the three treated plots and the control plot on July 15 (40 days after treatment) and again at harvesttime, August 12 (68 days after treatment).

Also, on June 1, 1967, aldicarb was applied to the soil around two plots of pear trees at the rates of 1 and 2 ounces of active ingredient per tree. Then on July 27 (50 days later) the plot treated with 1 ounce received an additional 1 ounce of active ingredient of aldicarb. The insecticide was washed into the soil as in 1966, but in this test each treated plot and the check plot consisted of three trees. Samples of 20 pears were taken at random from each of the three trees in the two treated and one untreated plots at harvesttime, August 22 (82 days after treatment). Samples from each plot were composited into a single sample. The pears from each plot were handled as for the 1966 samples.

Duplicate subsamples of 150 g. were taken from each of the diced composite samples, and blended for 4 minutes with 60 to 70 g. of anhydrous sodium sulfate and 450 ml. of distilled dichloromethane. The blended mixture was filtered through a glass wool plug into a flask containing 60 to 70 g. of anhydrous sulfate, shaken, and then filtered through a funnel containing a

cotton plug overlaid with sodium sulfate. The solution (300 ml.), which was equivalent to 100 g. of sample, was evaporated to dryness in a water bath at 40° C. with the aid of a gentle stream of air, and the residue was dissolved in 15 ml. of acetonitrile.

Sugarbeet Foliage, Crowns, and Roots

Aldicarb was applied twice to the foliage of sugarbeets in four randomized plots (95 X 44 feet) in eastern Washington, consisting of 24 rows of rill-irrigated sugarbeets 95 feet long. The first treatment (May 2, 1966) was a 6-inch-wide band of aldicarb applied to the top of the sugarbeet foliage of each plot at the rate of 2 pounds per acre of active ingredient. On June 1 (30 days later), a second application (1 pound of active ingredient per acre) was made to the tops of the foliage of each plot. In the second application, the treatment band width was increased to 12 inches to compensate for the increased growth of foliage.

On October 5, 126 days after the last treatment, eight sugarbeets were taken at random from a 43- X 27-foot area within the center of each plot. The samples were brought to the laboratory, thoroughly washed, and the beets from each plot were divided into foliage, crowns, and roots. The foliage and crowns were immediately frozen, and the roots were cut into elongated quarters before freezing and one-quarter of each root was saved for analysis. Before extraction, the samples of foliage, crowns, and roots were allowed to partially thaw and were chopped in a Buffalo chopper. From each of the chopped samples, two subsamples (150 g. each) were taken and prepared in the same way as the apples.

Cottonseed

In both 1966 and 1967, 1 to 4 pounds per acre of aldicarb was applied at planting time in the row or as a sidedress to plots of cotton. Table 1 shows the methods, rates, and dates of treatment and the dates of sampling. Samples of cotton were picked at random from the treated plots and ginned; the cottonseed was stored frozen until analysis. The seed was fractured into small particles in a Waring Blendor, and two subsamples of 100 g. of the ground seed were blended for 5 minutes with 20 to 30 g. of anhydrous sodium sulfate and 500 ml. of distilled dichloromethane. The blended mixture was filtered through a glass wool plug into a beaker, and the resulting solution was filtered through a funnel containing a cotton plug overlaid with sodium sulfate. The resultant filtrate was measured, transferred to a flask containing 5 grams of a 2:1 mixture of sodium sulfate and Hyflo Super Cel, and evaporated to dryness in a water bath (40° C.) with the aid of a gentle stream of air. The residue was dissolved in 40 ml. of acetonitrile.

CLEANUP PROCEDURE AND THE ANALYTICAL METHOD

The same cleanup procedure and analytical method was used for all crops. The procedure and the method are those of Maitlen and others (6). However, when apples and sugarbeets were analyzed, an interference was detected with the same retention time on the gas chromatograph as the sulfoxide of aldicarb This interference was not present in the controls; it was revealed by

Table 1.--Treatment of cottonseed with aldicarb and subsequent sampling of cotton

[1/ Gr, Granular applicator; No, Noble applicator; Ga, Gandy applicator; A, at planting; S, sidedress]

Treatment date	Treatment level with aldicarb	Days sampled after treatment	Method of treatment
	Pounds of active ingredient per acre		
1966			
Apr. 7	1/ 1.0	104	Gr, A
June 1	1/ 4.0	104	Gr, S
Apr. 7	1.0	159	Gr, A
May 10	1.0	150	No, A
June 4	3.0	109	Gr, S
	3.0	109	Gr, S
June 9	1.7	123	No, S
	3.0	123	No, S
June 11	3.0	119	Ga, S
June 12	1.0	121	No, A
	2.0	157	Ga, S
June 16	2.0	102	Gr, S
June 25	2.7	139	No, S
1967			
May 6	2.0	183	Gr, A
	1/ 1.0	137	Gr, A
June 21	1/ 1.0	137	Gr, S
	2.0	137	Gr, S
Sept. 15	3.0	60	Gr, S
	6.0	60	Gr, S

1/ Double application to the same plot; the number of days after treatment that samples were collected refers to the second application.

incorrect extraction p-values (2). Also, after the sulfoxide was oxidized to the sulfone, gas-liquid chromatography showed the interfering peak at the retention time of the sulfoxide. Consequently, the sulfoxide was oxidized and determined as the sulfone (6). The limit of sensitivity was 7 parts per billion on cottonseed and 10 p.p.b. on the other crops. All analytical results were substantiated by extraction p-values (2). Sulfone p-values were determined by partition between 20 ml. of water and 20 ml. of a solvent mixture of 60° to 90° petroleum ether (three parts) and chloroform (seven parts); sulfoxide p-values were determined with 20 ml. of water and 20 ml. of chloroform. The immiscible solvent pairs were in each case pre-equilibrated with each other.

Known amounts of aldicarb, its sulfoxide, and its sulfone were added at levels of 0.05, 0.10, and 0.50 parts per million to untreated samples of each crop, and the percentage recovery was determined. The data are summarized in table 2. Untreated control samples were also analyzed. Except for the untreated samples of pears, no "apparent" residues were found. The apparent residue in pears was 0.02 p.p.m. of aldicarb sulfoxide.

Table 2.--Average percentage recovery of aldicarb and its toxic metabolites from crops

Crop	Percentage recovery of --		
	Aldicarb	Sulfoxide of aldicarb	Sulfone of aldicarb
	Percent	Percent	Percent
Apples - - - - - - -	93	100	101
Pears:			
1966 - - - -	71	81	94
1967 - - - -	80	80	95
Sugarbeets:			
Foliage- - -	81	111	110
Crowns - - -	59	115	104
Roots- - - -	67	100	109
Cottonseed:			
1966 - - - -	85	80	103
1967[1/] - - -	96	85	70

1/ Determined at 0.02 p.p.m.

RESULTS AND DISCUSSION

The data of Metcalf and others (7) indicated that on cotton the sulfoxide and sulfone of aldicarb occur as residues to a greater extent than aldicarb. The results of our tests (table 3) extend this finding to apples, pears, and sugarbeets. In addition, our results show that both metabolites persisted significantly.

The data for pears for the 2 years are not exactly comparable because the number of days the pears were sampled after the application of aldicarb differs. The closest comparison can be made between the rate of 2 ounces per tree applied in 1966 when the pears, sampled 68 days after treatment, contained 0.31 p.p.m. of sulfoxide and 0.13 p.p.m. of sulfone versus the 2 ounces per tree treatment applied in 1967 when the pears, sampled 82 days after treatment, contained 0.21 p.p.m. of sulfoxide and 0.11 p.p.m. of sulfone. The

Table 3.--Residues of aldicarb, its sulfoxide and its sulfone in apples, pears, and sugarbeets[1/]

Crop and treatment level with aldicarb	Days sampled after application	Residues[2/]	
		Sulfoxide aldicarb	Sulfone aldicarb
Pounds of active ingredient per tree		P.p.m.	P.p.m.
Apples:[2/]			
0.1	143	0.08	0.04
.2	143	.23	.04
.4	143	.83	.14
Ounces of active ingredient per tree			
Pears (1966):[2/]			
1	40	.18	.07
1	68	.04	.03
2	40	.44	.14
2	68	.31	.13
4	40	.49	.31
4	68	.75	.29
Pears (1967):[2/]			
2	82	.21	.11
1[3/]	[4/] 82	.06	.03
Pounds of active ingredient per acre			
Sugarbeets, 2[5/]	[4/] 126	----	----
Foliage[6/]	---	.58	.86
Crowns[6/]	---	.04	.03
Roots[6/]	---	.03	.02

1/ On the basis of the percentage recovery found, all data have been corrected to 100%.

2/ Average of 2 replicates. Concentration of aldicarb was always less than 0.01 p.p.m.

3/ Plus 1 oz. per tree 50 days later.

4/ Days after the first application.

5/ Plus 1 lb. per acre 30 days later.

6/ Average of 4 field replicates, each of which was replicated twice in the laboratory.

agreement is excellent. Further, these data show that pears treated with aldicarb can be stored for over a year at 0° C. without significant loss of residues. In 1967 the double application of two 1-ounce-per-tree treatments resulted in less residue than the single application of 2 ounces per tree. Evidently the insecticide is translocated more readily earlier in the season than later.

Low residues were found in the roots and crowns of sugarbeets, whereas larger residues were found in the foliage. Because pulp left after the removal of the sugar from the sugarbeet roots is used for cattle feed, and the crowns and foliage are left in the field for grazing cattle, these residues are important. Dorough and Ivie (3) studied the fate of aldicarb fed to cows. When a cow was given a single feeding of 40 mg. of aldicarb in 2 pounds of grain (about 40 p.p.m. and equivalent to 0.1 mg. of aldicarb per kilogram of body weight), 90.2 percent of the aldicarb and its metabolites were detected in the urine, 2.9 percent in the feces, and 3.0 percent in the milk. The toxic sulfoxide and sulfone metabolites were detected in the milk samples taken 3, 6, and 12 hours after feeding, but not afterward; the peak level occurred in the 3-hour sample where total sulfoxide and sulfone residues of 0.01 p.p.m. were found.

The lowest residues were found on cottonseed, where they were below the limit of sensitivity of 7 p.p.b. for all except two samples from the 1967 test. The two replicates of sample 14 (table 1) from a double treatment of 1 pound per acre (May 6 and June 21) sampled 137 days after the first treatment contained 8 and <7 p.p.b. of the sulfone of aldicarb. The two replicates of sample 15, treated June 21 at 2 pounds per acre and sampled 137 days later, contained 13 and 16 p.p.b. of sulfone.

Table 4 shows the effect of aldicarb on two varieties of mites on apple trees during two growing seasons. The results obtained in 1966, when aldicarb was applied at 1, 2, and 4 pounds of the 10-percent granular formulation per tree on May 9, are compared with those obtained with the standard binapacryl treatment. At 2 and 4 pounds per tree, aldicarb controlled both species until the middle of August; at 1 pound per tree, control was achieved until the end of July. In 1967, control was achieved from June 1 to August 2 with a dose of 2 pounds per tree, while 1 pound per tree applied on June 1 and July 10 gave control 3 to 4 weeks longer.

Table 5 shows the efficacy of aldicarb against pear psylla. During the 1966 season the infestation was light so the effectiveness of the treatments must be judged from comparatively few insects. The treatment with 1 ounce of aldicarb was less effective than the Perthane spray, but treatments with 2 and 4 ounces were effective and held the psylla to very small numbers throughout the season.

ACKNOWLEDGMENTS

We are indebted to Wilma Mook, chemistry scientific aide at Yakima, Wash., for technical assistance with the chemical analysis, and to the Union Carbide Corp. for the cottonseed samples.

Table 4.--Number of McDaniel spider mites, (McD), Tetranychus mcdanieli McGregor, and European red mites (ERM), Panonychus ulmi (Koch), per leaf from apple trees treated with a 10-percent granular formulation of aldicarb

Treatment date and type	Treatment level	Type of mite	No. of mites found on indicated sampling dates[1/]						
			6/18	6/23	7/15	7/22	8/5	8/25	9/13
	Pounds per tree					1966			
May 9:									
Aldicarb- - -	1.0	McD	0.4	0.0	0.4	2.7	10.1	13.6	33.7
	1.0	ERM	.0	.0	.2	.0	.9	4.0	.5
	1.0	McD	.0	.0	.5	2.8	2.2	10.8	19.8
	1.0	ERM	.0	.0	.0	.3	3.0	3.5	.7
	4.0	McD	.0	.0	2.5	1.2	1.0	23.1	27.4
	4.0	ERM	.0	.0	.0	.0	2.7	2.8	.9
Binapacryl[2/]-	---	McD	.0	1.2	3.4	.2	.5	1.9	9.0
July 19:									
Binapacryl[2/]-	---	ERM	.0	.0	.1	.2	.8	3.0	6.6
						1967			
			6/21	7/3	7/12	8/2	8/18	9/12	
June 1:									
Aldicarb- - -	2.0	McD	0.0	0.3	0.2	8.0	15.4	53.2	
	2.0	ERM	1.4	2.6	9.2	2.8	.0	.0	
	1.0	McD	.2	1.3	4.0	7.7	2.7	24.1	
July 20:									
Aldicarb- - -	1.0	ERM	.0	3.2	4.5	.0	.0	.0	
July 19:									
Binapacryl[2/]-	---	McD	.2	.4	5.6	.0	1.1	4.8	
	---	ERM	2.7	36.6	38.6	.0	.0	.0	

1/ Counted with a brushing machine (5).

2/ A 50% wettable powder (0.5 lb.) in 1 gal. of spray.

Table 5.--Number of nymphs of pear psylla, Psylla pyricola Foerster, on samples of 50 pear leaves taken at various times during the pear-growing season after the trees were treated with aldicarb

Treatment date and type (1966)	Treatment level	No. of psylla found on indicated sampling dates[1/]						
		6/26	6/30	7/13	7/22	7/28	8/5	8/25
	Ounces per tree							
May 6:								
Aldicarb - - -	1.0	4	15	7	5	13	18	3
	2.0	0	0	1	0	0	3	3
	4.0	0	0	0	0	0	2	4
June 28:								
Perthane[2,3/] -	---	66	15	4	1	5	3	11
July 19:								
Oil[3,4/] - - - -	---							

1/ Counted with a brushing machine (5).

2/ A mixture of 1,1-dichloro-2,2-bis(p-ethylphenyl)ethane (95%) and released reaction products (5%); a Perthane emulsion (1 qt., containing 1 lb. of Perthane per quart of emulsion) was applied in 1 gal. of spray.

3/ The Perthane and oil were applied to the same trees on the dates indicated.

4/ 1 gal. of Volck Supreme Oil (Chevron Oil Co.) was applied in 100 gal. of spray.

LITERATURE CITED

(1) Anonymous.
1965. Temik 10G experimental systemic pesticide. Union Carbide Tech. Bul. F-40977B, 16 pp.

(2) Beroza, M., and Bowman, M. C.
1965. Identification of pesticides at nanogram level by extraction p-values. Jour. Analyt. Chem. 37(2): 291-292.

(3) Dorough, H. W., and Ivie, G. W.
1968. Temik-S^{35} metabolism in a lactating cow. Jour. Agr. and Food Chem. 16(3): 460-464.

(4) Frear, D. E. H.
1963. Pesticide index. 231 pp. State College, Pa.

(5) Henderson, C. F., and McBurnie, H. V.
1942. Sampling technique for determining populations of the citrus red mite and its predators. U.S. Dept. Agr. Cir. 671, 15 pp.

(6) Maitlen, J. C., McDonough, L. M., and Beroza, M.
1968. Determination of residues of 2-methyl-2-(methylthio)propionaldehyde O-(methylcarbamoyl)oxime (UC-21149, Temik), its sulfoxide, and its sulfone by gas chromatography. Jour. Agr. and Food Chem. 16(4): 549-553.

(7) Metcalf, R. L., Fukuto, T. R., Collins, C., and others.
1966. Metabolism of 2-methyl-2-(methylthio)propionaldehyde O-(methylcarbamoyl)oxime in plant and insect. Jour. Agr. and Food Chem. 14(6): 579-584.

(8) Tamaki, G., Halfhill, J. E., and Maitlen, J. C.
1969. The influence of UC-21149 and the aphidiid parasite Aphidius smithi on populations of the pea aphid. Jour. Econ. Ent. 62(3): 678-682.

(9) Tashiro, H., Chambers, D. L., Shaw, J. G., and others.
1969. Systemic activity of UC-21149 against the citrus red mite, citrus thrips, California red scale, and spirea aphid on non-bearing orange trees. Jour. Econ. Ent. 62(2): 443-447.

(10) Weiden, M. H. J., Moorefield, H. H., and Payne, L. K.
1965. O(methylcarbamoyl)oximes: a new class of carbamate insecticides-acaricides. Jour. Econ. Ent. 58(1): 154-155.